

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34863 A1

(51) International Patent Classification⁷: C10G 19/00, 29/20, 27/00

(21) International Application Number: PCT/US01/32211

(22) International Filing Date: 16 October 2001 (16.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/697,200 26 October 2000 (26.10.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: REMOVAL OF MERCAPTANS FROM HYDROCARBON STREAMS USING IONIC LIQUIDS

(57) Abstract: Methods for removing mercaptans from hydrocarbons streams, for example crude oil and natural gas, are provided. The methods use basic metal salts which react with mercaptans to form mercaptides. The metal salts are dissolved or suspended in ionic liquids, which tend to have virtually no vapor pressure. After the mercaptides are adsorbed into the ionic liquid, the demercaptanized hydrocarbon stream can be removed, for example by distillation, decantation or gravity separation. Then the mercaptides can be oxidized, for example, by exposure to air, to form disulfides. The disulfides are insoluble in the ionic liquids, and can be readily removed. Sodium hydroxide is a preferred salt. Non-water reactive ionic liquids are preferred. The mercaptan-containing hydrocarbon stream can be in the gas phase or in the liquid phase. The flow of hydrocarbon stream over/through the ionic liquid can be for example, co-current, counter-current, or staged in stirred tanks, with countercurrent being preferred.



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REMOVAL OF MERCAPTANS FROM HYDROCARBON STREAMS USING IONIC LIQUIDS

Field of the Invention

5 The present invention is in the field of organic chemistry, in particular removal of mercaptans from hydrocarbon streams.

Background of the Invention

10 There are many product streams in petroleum chemistry which are contaminated with mercaptans (RSH). These compounds are odorous and tend to be corrosive and toxic. They contribute to acid rain, and also tend to poison a number of catalysts used in hydrocarbon conversions. Accordingly, it is important to remove mercaptans from many hydrocarbon streams, or at least convert them to less toxic and corrosive compounds such as disulfides (RSSR') where R and R' can be different hydrocarbon groups. An excellent review of the traditional methods of
15 removing mercaptans and hydrogen sulfide from petroleum streams is found in Chemical Technology of Petroleum by William A. Gruse and Donald R. Stevens, 3rd Edition, McGraw-Hill Book Company, Inc., pages 301-304.

 Mercaptans are commonly removed using a "sweetening" or "extractive sweetening" process. This type of process generally involves reacting mercaptans (RSH) with caustic solutions
20 (NaOH) to form water and mercaptides (NaSR). The mercaptides are then oxidized, usually with air, to form disulfides (RSSR'), which regenerates the caustic. The disulfides are for the most part immiscible in the caustic and can be separated by density differences. The disulfides can either be disposed of or, in some cases, blended with the original product stream.

 The caustic is generally recycled until it reaches a low enough concentration where it is no
25 longer effective at adsorbing the mercaptans. The concentration of caustic decreases in part because the water formed in the reaction of the mercaptan with caustic generates water, which remains with the caustic. Dissolved water in the crude oil can also cause a decline in the concentration of the caustic. The result is that the caustic must continuously be disposed of and replaced.

30 It is particularly difficult to remove low molecular weight mercaptans such as ethyl and methyl mercaptan from crude oils. These mercaptans must be reduced to a few ppm for them to be acceptable for shipping on tankers. When caustic solutions are mixed with crude oil, emulsions often form. To avoid direct mixing of caustic with crude, the light portion of the crude can be

distilled, the mercaptans removed, and the product blended with the crude. This option requires using expensive distillation facilities to remove the light portion of the crude.

The oxidation of the mercaptides to disulfides and regenerated caustic can be done with a variety of oxidants (air, pure oxygen, enriched air, chemical oxidants such as hydrogen peroxide) or mixtures thereof. However, air is the most commonly used oxidant because of its low cost. The oxidation of the mercaptides can be done without a catalyst, but the reaction tends to be slow. It is generally preferred to incorporate a catalyst to accelerate the oxidation of the mercaptides. These catalysts are typically metals, and the most common metals are lead (typically as PbS), copper (typically as a copper chloride), or a phthalocyanine complex of copper, iron, nickel or cobalt, preferably cobalt. The preparation and use of phthalocyanine complexes for mercaptan oxidation is described in U.S. Pat. No. 5,880,279; U.S. Pat. No. 5,849,656, U.S. Pat. No. 5,741,415, and U.S. Pat. No. 5,683,574 to Mazgarov et al. A particularly effective phthalocyanine complex involves cobalt phthalocyanine complexes with electron withdrawing substituents on the phthalocyanine ring. Particularly effective electron withdrawing substituents include a halogen (preferably chlorine) and sulfate groups as described in U.S. Pat. No. 5,880,279.

The extraction of the mercaptans and the oxidation of the mercaptides can be done in one or two stages. The advantage of the use of one stage is primarily lower cost, but the disadvantages include the mixing of the oxidant and petroleum product, and the blending of the mercaptan reaction product disulfides with the petroleum product. The advantages of use to two separate stages is the avoidance of mixing the oxidant and the petroleum product, and the separation of the disulfide reaction product, but the disadvantage is higher cost.

Mercaptans can be removed from whole crudes by contacting the crude oil with a caustic mixture that includes a cobalt phthalocyanine complex and air, as described in U.S. Pat. No. 5,683,574. The cobalt phthalocyanine complexes are selected to avoid formation of emulsions. The caustic/cobalt phthalocyanine solution simultaneously adsorbs the mercaptans and reacts them to form disulfides, which remain in the crude. The caustic and phthalocyanine complexes can be partially recovered using a separation system. However, this technology has various technical limitations. For example, the introduction of air directly in with the crude causes concerns over safety, and when nitrogen from the air is released from the crude, light (C₄-) hydrocarbons are also purged. This not only results in a loss of crude, but also causes a safety hazard and a disposal problem. Also, since the reaction is essentially stoichiometric, the amount of caustic and cobalt catalyst that must be used increases, often to the point where it is not economically viable to treat the crude.

It would be advantageous to have efficient methods for removing mercaptans from hydrocarbon streams without creating a waste caustic stream, preferably without introducing air to the hydrocarbon streams. The present invention provides such methods.

5

Summary of the Invention

Methods for removing mercaptans from hydrocarbon streams, preferably crude oil, are provided. The methods involve forming a solution of a basic metal salt such as sodium hydroxide in an ionic liquid, preferably a non-water reactive ionic liquids, and contacting the ionic liquid solution with a hydrocarbon stream in a manner which contacts mercaptans in the hydrocarbon stream with the basic metal salt. The resulting mercaptide salts are either dissolved or dispersed in the ionic liquid, dissolved in the reaction water, or precipitated. Generally they are dissolved in the ionic liquid. The resulting de-sulfurized hydrocarbon feedstream can be separated from the ionic liquid, for example by distillation, decantation or gravity separation.

The caustic can be recovered by oxidizing the mercaptides to form disulfides, preferably using air or oxygen. The oxidation can be promoted by a catalyst, preferably a metal phthalocyanine complex where the metal is preferably cobalt and the phthalocyanine ring includes halogens, preferably chlorine, as described in U.S. Pat. No. 5,880,279. The catalyst can be fixed on a solid support or, alternatively, dissolved or dispersed in the ionic liquid.

The disulfides are non-ionic and tend to be insoluble in the ionic liquids. Accordingly, the disulfides can be readily removed, for example via distillation, decantation or gravity separation. Additionally, the disulfides can be removed by stripping with steam, air or other suitable gas streams, or by extraction in a suitable solvent, for example a hydrocarbon solvent. The de-sulfurized ionic liquid can then be recycled.

The reaction water produced by the reaction of caustic and mercaptans tends to be insoluble in the ionic liquids. The water can also be removed by distillation, decantation or gravity separation. If the mercaptide is not particularly soluble in the reaction water, the water can be removed by decantation or gravity separation before the oxidation step. The basic metal salt can be kept reasonably concentrated in the ionic liquid without unwanted dilution in water using the methods described herein.

The mercaptan-containing hydrocarbon stream can be in the gas phase or in the liquid phase. The flow of hydrocarbon stream over/through the ionic liquid can be, for example, co-current, counter-current, or staged in stirred tanks, with countercurrent being preferred.

It should also be recognized that this approach is effective in removing hydrogen sulfide from petroleum products.

Brief Description of the Drawings

Figure 1 is a schematic illustration of a mercaptan removal process using the method described herein.

5

Detailed Description of the Invention

Methods for removing mercaptans from hydrocarbon streams, preferably crude oil, are provided. As used herein, the term "adsorption" is used to describe the movement of mercaptans out of hydrocarbon streams and into ionic liquids in the form of mercaptides.

10

Mercaptans

Mercaptans are C₁₋₅₀ mercaptans (carbon-containing compounds that contain a -SH group), more preferably C₁₋₁₀ (cyclic, linear, branched and aromatic) mercaptans. They may include other functional groups, such as hydroxy groups, carboxylic acid groups, heteroatoms, and the like, provided that such groups do not react with either the base (typically sodium hydroxide) or the ionic liquid.

15

Hydrocarbon Feedstreams

The hydrocarbon feedstreams include crude oil feedstreams and natural gas feedstreams. The hydrocarbon stream can include a C₆- fraction. The hydrocarbon stream can include more than about 50% by weight methane, ethane, propane, butane or combinations thereof.

20

Where the hydrocarbon feedstreams include relatively high levels of sulfur impurities, and the feedstream is amenable to hydrotreatment or other means well known to those of skill in the art, such as extractive Merox, such methods can be used to reduce the level of sulfur impurities, and residual mercaptans can be removed using the methods described herein.

25

Basic Salts

The basic salts can be virtually any base capable of reacting with mercaptans to form mercaptides. Examples include alkali metal and alkaline earth hydroxides, carbonates and bicarbonates. Sodium hydroxide is a preferred basic salt.

30

The concentration of the basic salt in the ionic liquid is typically at least about 0.5 moles of salt per liter of solvent, and preferably at least about 2 moles of salt per liter of solvent.

It does not matter whether the salts are dissolved or merely suspended in the ionic liquids for them to function as intended. It is preferred, however, to select combinations of ionic liquids

and basic salts that form a solution rather than a suspension, as the solids in suspensions tend to settle and become non-available for the reaction.

The salts are able to react with the mercaptans at a variety of concentrations. At relatively high concentrations, the mercaptides may precipitate from solution. If this precipitation is not desirable, more dilute solutions/dispersions should be used. However, this precipitation may be desirable and allow one to separate various mercaptides by precipitation and subsequent filtration.

The extent of mercaptan removal is a least 10%, preferably more than 50% and most preferably more than 90%. The product disulfides can be either produced as a separate stream or blended with the hydrocarbon product. Methods of measuring mercaptans in petroleum products include gas chromatography (especially when coupled with a sulfur sensitive elemental detector). ASTM D3227 can also be used to measure mercaptans in gasoline, jet and distillate boiling range products. If quantitative measurements of mercaptans are not possible (for example in heavy crude oils), the extent of mercaptan removal can be judged by an improvement in the copper strip corrosion test (ASTM D130) of at least one value.

Ionic Liquids

Ionic liquids are organic compounds that are liquid at room temperature. They differ from most salts in that they have very low melting points. They tend to be liquid over a wide temperature range, and are not soluble in non-polar hydrocarbons. Depending on the anion, they tend to be immiscible with water, and are highly ionizing (but have a low dielectric strength). Ionic liquids have essentially no vapor pressure. Most are air- and water-stable, and they are used herein as a catalyst and/or solvent for the Diels-Alder reaction between the diene and the dienophile.

The properties of the ionic liquids can be tailored by varying the cation and anion. Ionic liquids and their commercial applications are described, for example, in *J. Chem. Tech. Biotechnol.*, 68:351-356 (1997); *Chem. Ind.*, 68:249-263 (1996); *J. Phys. Condensed Matter*, 5:(supp 34B):B99-B106 (1993); *Chemical and Engineering News*, March 30, 1998, 32-37; *J. Mater. Chem.*, 2627-2636 (1998); and *Chem. Rev.*, 99:2071-2084 (1999), the contents of which are hereby incorporated by reference.

Many ionic liquids are formed by reacting a nitrogen-containing heterocyclic ring, preferably a heteroaromatic ring, with an alkylating agent (for example, an alkyl halide) to form a quaternary ammonium salt, and performing ion exchange or other suitable reactions to form ionic liquids. Examples of suitable heteroaromatic rings include pyridine, substituted pyridines, imidazole, substituted imidazoles, pyrrole and substituted pyrroles. Suitable substituents include,

for example, straight, branched, or cyclic alkyl groups, preferably a methyl group, alkyl chains containing a terminal alcohol group, alkyl groups containing heteroatoms such as oxygen, nitrogen and/or sulfur. The substituents can be in any position on the heteroaromatic ring, but in the case of pyridine, is preferably in the para (or 4) position.

5 These rings can alkylated with virtually any straight, branched or cyclic C₁₋₂₀ alkyl group, but preferably the alkyl groups are C₁₋₁₆ groups, since groups larger than this tend to produce low melting solids rather than ionic liquids. Various triarylphosphines, thioethers, and cyclic and non-cyclic quaternary ammonium salts have also been used. Counterions which have been used
10 include chloroaluminate, bromoaluminate, gallium chloride, tetrafluoroborate, tetrachloroborate, hexafluorophosphate, nitrate, trifluoromethane sulfonate, methylsulfonate, p-toluenesulfonate, hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate, tetrabromoaluminate, perchlorate, hydroxide ion, copper dichloride anion, iron trichloride anion, zinc trichloride anion, as well as various lanthanum, potassium, lithium, nickel, cobalt, manganese, and other metal ions.

 Certain low melting solids can also be used in place of ionic liquids, depending on the
15 particular separation to be effected. Low melting solids are generally similar to ionic liquids but have melting points between room temperature and about 212°C or are liquid under the process conditions. The use of low melting solids can be preferred if the density of the products and the ionic liquid are similar and it becomes difficult to phase separate products from the ionic liquids. In such a case, the low melting solid can be crystallized and separated from the products. As used
20 herein, the term "ionic liquid" is intended to include low melting solids unless otherwise specified.

 The ionic liquids can either be neutral, acidic or basic. However, relatively acidic ionic liquids (chloroaluminate salts) tend to be water-reactive, whereas neutral ionic liquids (for example, tetrafluoroborate or hexafluorophosphate salts) tend to be non-water reactive. Since water is generated, it can be preferable to use non-water reactive ionic liquids, particularly if large
25 amounts of mercaptans are to be removed. Neutral ionic liquids are also preferred if the hydrocarbon stream includes acid-sensitive components, for example normal alpha olefins, which are prone to isomerization.

 In one embodiment, a library of ionic liquids is prepared, for example by preparing various alkyl derivatives of the quaternary ammonium cation, and/or varying the associated anions.
30 The acidity of the ionic liquids can be adjusted, for example by varying the molar equivalents and combinations of Lewis acids.

Methods for Removing Mercaptans from Hydrocarbon Streams

The methods involve forming a solution of a basic metal salt such as sodium hydroxide in

an ionic liquid, preferably a non-water reactive ionic liquids, and contacting the ionic liquid solution with a hydrocarbon stream in a manner which contacts mercaptans in the hydrocarbon stream with the basic metal salt. The resulting mercaptide salts are either dissolved or dispersed in the ionic liquid, dissolved in the reaction water or precipitated. Preferably they are dissolved in the ionic liquid. The resulting de-sulfurized hydrocarbon feedstream can be separated from the ionic liquid, for example by distillation, decantation or gravity separation.

If low sulfur products are desired, it is important that contact with air be minimized during this step to avoid oxidation of the mercaptides to disulfides, which may dissolve back into the hydrocarbon stream. Contact with air can be minimized, for example by reacting the mercaptans with the basic metal salts in an inert atmosphere, for example nitrogen or argon.

If low sulfur products are not relevant but reduction of mercaptans is desired, the hydrocarbon stream, the ionic liquid incorporating the basic metal salt, and an oxidant can be contacted simultaneously. In this case the product disulfide will be incorporated into the product. A catalyst to promote generation of the basic metal salt can also be incorporated as well (either dissolved in the ionic liquid, dispersed in the ionic liquid or supported on a solid). In one embodiment, low melting solids are used in place of ionic liquids, and the desulfurized hydrocarbon feedstream is recovered following precipitation of the low melting solid. In this embodiment, the low melting solid must be a liquid at the temperature at which the mercaptans are adsorbed, to permit contact of the mercaptans with the basic salt.

Methods for Oxidizing Mercaptides in Ionic Liquids

The caustic can be recovered by oxidizing the mercaptides to form disulfides, preferably using air or oxygen. The oxidation can be promoted by a catalyst, preferably a metal phthalocyanine complex where the metal is preferably cobalt and the phthalocyanine ring includes halogens, preferably chlorine. The preferred catalyst is described in U.S. Pat. No. 5,880,279. The catalyst can be fixed on a solid support or, alternatively, dissolved or dispersed in the ionic liquid.

The disulfides are non-ionic, and tend to be insoluble in the ionic liquids. Accordingly, the disulfides can be readily removed, for example via distillation, decantation or gravity separation. Additionally, the disulfides can be removed by stripping with steam, air or other suitable gas streams, or by extraction in a suitable solvent, for example a hydrocarbon solvent. The resulting de-sulfurized ionic liquids can be recycled.

The water formed by reacting hydroxide ions with mercaptans tends to be insoluble in the ionic liquids. The water can also be removed by distillation, decantation or gravity separation. Decantation and gravity separation may tend to remove caustic and/or mercaptide salts from the

ionic liquid. Accordingly, distillation, preferably under reduced pressure, is a preferred method for removing the water. Alternatively, if the mercaptide is not particularly soluble in the reaction water, the reaction water can be removed before the oxidation step. The basic metal salt can be kept reasonably concentrated in the ionic liquid without unwanted dilution in water using the methods described herein.

The mercaptan-containing hydrocarbon stream can be in the gas phase or in the liquid phase. The flow of hydrocarbon stream over/through the ionic liquid can be, for example, co-current, counter-current, or staged in stirred tanks, with countercurrent being preferred.

The method is shown in more detail in Figure 1. As shown in Figure 1, a hydrocarbon with mercaptan (RSH) impurities is introduced to a contactor (10) that contains a non-water reactive ionic liquid and caustic. The resulting mercaptide is then either dispersed or dissolved in the ionic liquid, precipitated, or dissolved in the resulting aqueous phase. The reaction mixture is sent to a separator (20) where a purified hydrocarbon stream can be separated. The ionic liquid and, optionally, reaction water are sent to an oxidation reactor (30) where disulfide is formed and caustic is regenerated. The disulfide and reaction water can then be removed, regenerating the ionic liquid and caustic. The regenerated ionic liquid and caustic are then recycled to the contactor (10).

Combinatorial Chemistry Approaches

A combinatorial approach can be used to identify optimum ionic liquids and/or basic salts for removing mercaptans from various hydrocarbon streams. An advantage to the combinatorial approach is that the choice of ionic liquid, basic salt and the like can be tailored to specific applications.

The scale of the mercaptan removal in combinatorial chemistry is preferably in the range of about 1 mg to 200 g, more preferably between one mg and 10 g, although the scale can be modified as desired depending on the equipment used. Those of skill in the art can readily determine appropriate sets of reactions and reaction conditions to generate and/or evaluate the libraries of interest.

The ionic liquids can be laid out in a logical fashion in multi-tube arrays or multi-well plates in the form of arrays of ionic liquids. Preferably, the ionic liquids all have a central core structure and have various modifications that permit the identification of structure-activity relationships with which to determine optimum compounds for a particular use. The basic metal salts or combinations thereof can also be laid out in a logical fashion, for example in arrays. In a preferred embodiment, an A x B array is prepared with various combinations of ionic liquids and

basic metal salts. However, it is also possible to evaluate a single ionic liquid with a plurality of metal salts, optionally at different concentrations, and then repeat the process as desired with a plurality of different ionic liquids.

5 The ability of the particular combination of ionic liquid and metal salt at performing a desired mercaptan removal can be measured and correlated to specific combinations. The array can be ordered in such a fashion as to expedite synthesis and/or evaluation, to maximize the informational content obtained from the testing and to facilitate the rapid evaluation of that data. Methods for organizing libraries of compounds are well known to those of skill in the art, and are described, for example, in U.S. Patent No. 5,712,171 to Zambias et al. Such methods can readily
10 be adapted for use with the ionic liquids and basic metal salts described herein.

By screening multiple synthetic variations of a core molecule, the selection of the optimal candidate is more a function of the data collection method than the "rational" basis for selecting a useful ionic liquid and/or metal salt. The desired physical and chemical properties for the ionic liquid, when used as a solvent or dispersing agent for a particular metal salt, and for removing a
15 particular mercaptan from a particular hydrocarbon stream, can be rapidly optimized, and directly correlated with the structural changes within a particular array or sub-array.

The ionic liquids are typically formed by first forming a desired (cyclic, non-cyclic or aromatic) quaternary ammonium salt, and then combining the salt with an appropriate anion precursor (typically a metal salt such as aluminum chloride, zinc chloride, sodium
20 hexafluorophosphate, sodium tetrafluoroborate, hexafluorophosphoric acid, tetrafluoroboric acid and the like). Side products salts can be removed, for example by filtration or, in cases where the anion precursor was an acid, the acid side products such as HCl can be removed by extraction or by gently heating the ionic liquid under vacuum.

The mercaptan removal using the ionic liquids/metal salts in the libraries generally involve
25 contacting appropriate mixtures of mercaptans and hydrocarbons with the ionic liquids/basic metal salts in the tubes or wells in the multi-tube rack or multi-well plate, and allowing the mercaptide formation to take place. The formation of the mercaptide, and desulfurization of the hydrocarbon stream, can be analyzed, for example by GC by following mercaptan removal. The presence or absence of mercaptans can be evaluated, for example using GC, to determine the success of the
30 particular combination of ionic liquid and basic metal salt.

Robotic arms and multi-pipet devices are commonly used to add appropriate reagents to the appropriate tubes in multi-tube racks or wells in multi-well plates. Preferably, the chemistry is performed in an inert atmosphere to avoid oxidation of mercaptides to form disulfides before the

desulfurized hydrocarbon stream is removed. This can be done, for example, by covering the tubes with a rubber septum to avoid contamination, and adding the reagents via injection.

In one embodiment, the mercaptan removal is carried out via computer control. The identity of each of the ionic liquids and basic metal salts can be stored in a computer in a "memory map" or other means for correlating the data regarding the chemical reactions to the ionic liquids in the multi-tube racks or multi-well plates.

Alternatively, the chemistry can be performed manually, preferably in multi-tube racks or multi-well plates, and the information stored, for example on a computer.

Any type of multi-well plate or multi-tube array commonly used in combinatorial chemistry can be used. Preferably, the number of wells or tubes is in excess of 30, and there is a tube in at least 60 percent of the positions in each multi-tube array. The shape of the rack is not important, but preferably, the rack is square or rectangular. The tubes can be made, for example, from plastic, polymers, glass or metal such as stainless steel, depending on the type of anions used in the ionic liquid or in the metal salt.

Any type of liquid handler that can add reagents to, or remove reagents from, the wells and/or tubes can be used. Suitable liquid handlers are prepared, for example by Tecan. Many involve the use of robotic arms and robotic devices. Suitable devices are well known to those of skill in the art of combinatorial chemistry, and include those by Zymart, Gilson, Hamilton, Bodhan and Tecan.

Any device that can take samples from the individual wells and/or tubes and analyze the resulting hydrocarbon phase can be used. Preferably, the device is a chromatographic device such as an analytical or preparative scale HPLC, GC or column chromatography, although other devices can be envisioned depending on the chemistry performed. Since the ionic liquid is non-volatile, the sample is preferably taken from the hydrocarbon phase, which is immiscible with the ionic liquid.

Preferably, in those embodiments in which a chromatographic column (HPLC, GC or column chromatography) is used, the device has the ability to identify when the compound of interest is eluting from the column. Various means have commonly been used to identify when compounds of interest are eluting from a column, including UV, IR, TLC, GC-MS, FID, NMR, ELSD, nitrogen detection and the like. Any of these means and others known to those of skill in the art can be used, alone or in combination. However, when petroleum chemistry is being evaluated, the product stream often does not include UV-active compounds. In this type of embodiment, the analytical equipment preferably includes an ELSD detector.

The entire eluent from the chromatographic columns described above can be sent through an appropriate detector and then to a mass spectrometer. When sample collection is desired, it can begin when the UV or mass spectrometry signal indicates the presence of the eluting compound, and can end when the UV signal indicates that the compound has finished eluting from the column. Mass spectrometry can verify that the eluted compound is really the compound of interest. In some embodiments, it is preferred to use a combination of GC and MS, particularly if the mercaptans and various hydrocarbon components elute from the GC column at similar rates.

The device preferably includes a computer system capable of storing information regarding the identity of the ionic liquids, metal salts and the product streams obtained when combinations of ionic liquids and basic metal salts are used to remove the mercaptans. Software for managing the data is stored on the computer. Relational database software can be used to correlate the identity of the ionic liquids, the metal salts, and the analytical data from each product stream. Numerous commercially available relational database software programs are available, for example from Oracle, Tripos, MDL, Oxford Molecular ("Chemical Design"), IDBS ("Activity Base"), and other software vendors.

Relational database software is a preferred type of software for managing the data obtained during the processes described herein. However, any software that is able to create a "memory map" of the ionic liquids in the tubes and correlate that information with the information obtained from the chemical reactions can be used. This type of software is well known to those of skill in the art.

The present invention will be better understood with reference to the following non-limiting example.

Example: Synthesis of Neutral Ionic Liquids

A variety of quaternary amine ionic liquid precursors were prepared as follows. 1-Methylimidazole was measured into a stainless-steel autoclave along with a slight molar excess of 1-chlorobutane. The autoclave was sealed, pressurized with 75 psig of nitrogen, and heated to 90°C for 18 h. The autoclave was then cooled to room temperature and the contents were placed on a rotary evaporator at 95°C for several hours to remove any unreacted chlorobutane and 1-methylimidazole. A ¹H NMR of the product indicated the formation of 1-butyl-3-methylimidazolium chloride (bmim⁺Cl⁻). The reaction was repeated with 1-chlorohexane to give 1-hexyl-3-methylimidazolium chloride (hmim⁺Cl⁻). This general procedure was repeated with pyridine to give the ionic liquid precursors N-butylpyridinium chloride (butpyr⁺Cl⁻) and

N-hexylpyridinium chloride ($\text{hexpyr}^+\text{Cl}^-$), although a higher reaction temperature (130°C) was required to achieve high yields.

Two different procedures were used for conducting an anion exchange reaction to give a neutral ionic liquid. In one procedure, the precursor is dissolved in acetone and reacted with the sodium salt of the desired anion (NaBF_4 or NaPF_6). In the other procedure, the precursor is dissolved in water and reacted with the acid form of the anion (HBF_4 or HPF_6). The precursor hmim^+Cl^- was used to make the ionic liquid $\text{hmim}^+\text{PF}_6^-$ by both procedures. The miscibility of the resulting ionic liquid with water was greatly influenced by the route of synthesis. The ionic liquid made by the acid route was immiscible with water, while the ionic liquid made using the sodium salt was miscible with water. While not wishing to be bound to a particular theory, it is believed that this change in miscibility with water is due to the presence of residual NaCl in the liquid made via the salt route.

The acid procedure was then used to generate a variety of ionic liquids using the precursors synthesized above, as well as additional precursors purchased from commercial suppliers. These reactions are summarized in Table 1. Not all of the combinations resulted in the formation of room temperature ionic liquids. Highly symmetric cations (Me_4N^+) and cations with long alkyl chains ($\text{C}_{16}\text{NMe}_3^+$) tend to give solid products with high melting points ($>100^\circ\text{C}$). The reactions that did not result in room temperature ionic liquids are shown in Table 2.

Table 1. Neutral Ionic Liquids

Ionic Liquid Precursor	Anion Source	Ionic Liquid
bmim ⁺ Cl ⁻	HBF ₄	bmim ⁺ BF ₄ ⁻
bmim ⁺ Cl ⁻	HPF ₆	bmim ⁺ PF ₆ ⁻
hmim ⁺ Cl ⁻	NaBF ₄	hmim ⁺ BF ₄ ⁻
hmim ⁺ Cl ⁻	HBF ₄	hmim ⁺ BF ₄ ⁻
hmim ⁺ Cl ⁻	NaPF ₆	hmim ⁺ PF ₆ ⁻
hmim ⁺ Cl ⁻	HPF ₆	hmim ⁺ PF ₆ ⁻
hexpyr ⁺ Cl ⁻	HBF ₄	hexpyr ⁺ BF ₄ ⁻
hexpyr ⁺ Cl ⁻	HPF ₆	Hexpyr ⁺ PF ₆ ⁻ (mp = 38.7 1C)
(C ₈ H ₁₇) ₃ MeN ⁺ Cl ⁻	HBF ₄	(C ₈ H ₁₇) ₃ MeN ⁺ BF ₄ ⁻ (mp = 58.8°C)
(C ₈ H ₁₇) ₃ MeN ⁺ Cl ⁻	HPF ₆	(C ₈ H ₁₇) ₃ MeN ⁺ PF ₆ ⁻
Bu ₂ Me ₂ N ⁺ Cl ⁻	HBF ₄	Bu ₂ Me ₂ N ⁺ BF ₄ ⁻ (mp = 75.1 1C)

bmim = 1-butyl-3-methylimidazolium

hexpyr = N-hexylpyridinium

hmim = 1-hexyl-3-methylimidazolium

5

Table 2. Reactions which did not result in room temperature ionic liquids

Ionic Liquid Precursor	Anion Source	Solid Product
Me ₃ NH ⁺ Cl ⁻	HBF ₄	Me ₃ NH ⁺ BF ₄ ⁻ (mp = 183°C)
Me ₃ NH ⁺ Cl ⁻	HPF ₆	Me ₃ NH ⁺ PF ₆ ⁻
Me ₄ N ⁺ Cl ⁻	HPF ₆	Me ₄ N ⁺ PF ₆ ⁻
Me ₄ N ⁺ Cl ⁻	NaBF ₄	Me ₄ N ⁺ BF ₄ ⁻
Bu ₂ Me ₂ N ⁺ Cl ⁻	HPF ₆	Bu ₂ Me ₂ N ⁺ PF ₆ ⁻ (mp = 154.5°C)
(C ₁₆ H ₃₃)Me ₃ N ⁺ Cl ⁻	HBF ₄	(C ₁₆ H ₃₃)Me ₃ N ⁺ BF ₄ ⁻
(C ₁₆ H ₃₃)Me ₃ N ⁺ Cl ⁻	HPF ₆	(C ₁₆ H ₃₃)Me ₃ N ⁺ PF ₆ ⁻ (mp = 131.7°C)
hexPPh ₃ ⁺ Br ⁻	NaPF ₆	HexPPh ₃ ⁺ PF ₆ ⁻

hexPPh₃ = hexyltriphenylphosphonium

WHAT IS CLAIMED IS:

1. A method for removing mercaptans from hydrocarbon feedstreams comprising:
 - a) adding a mercaptan-containing hydrocarbon feedstream to an ionic liquid solution or dispersion of one or more basic metal salts to form mercaptides, where the mercaptides are
5 either precipitated from solution or are dissolved or dispersed in the ionic liquid; and
 - b) separating the resulting de-mercaptanized hydrocarbon feedstream from the ionic liquid.
2. The method of claim 1, wherein the de-mercaptanized hydrocarbon feedstream is separated from the ionic liquid by distillation, decantation or gravity separation.
- 10 3. The method of claim 1, wherein the basic metal salts comprise an alkali metal or alkaline earth salt.
4. The method of claim 1, wherein the basic metal salts comprise sodium or potassium hydroxide.
5. The method of claim 1, wherein the ionic liquid is a non-water-reactive ionic liquid.
- 15 6. The method of claim 1, wherein the ionic liquid comprises tetrafluoroborate or hexafluorophosphate ions.
7. The method of claim 1, wherein the ionic liquid comprises quaternary amines with three or more methyl groups.
8. The method of claim 1, wherein the hydrocarbon stream comprises a C₆- fraction.
- 20 9. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight methane.
10. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight ethane.
11. The method of claim 1, wherein the hydrocarbon stream includes more than about
25 50% by weight propane.
12. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight butane.
13. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight LPG.
- 30 14. The method of claim 1, wherein the hydrocarbon feedstream is crude oil.
15. The method of claim 1, wherein the ionic liquid has a melting point at or below 100°C.
16. The method of claim 1, wherein the mercaptans comprise methyl and/or ethyl mercaptan.

17. The method of claim 1, further comprising oxidizing the mercaptides to form disulfides.
18. The method of claim 17, wherein the oxidation is promoted by a catalyst.
19. The method of claim 18, wherein the catalyst is a metal.
- 5 20. The method of claim 19, wherein the metal is selected from the list of lead, copper, iron, nickel, cobalt or combinations thereof.
21. The method of claim 20, wherein the metal is present in the form of a phthalocyanine complex.
22. The method of claim 21, wherein the metal in the phthalocyanine complex is cobalt.
- 10 23. The method of claim 22, wherein the metal phthalocyanine complex comprises halogens in the phthalocyanine ring.
24. The method of claim 23, wherein the halogens comprise chlorine.
25. The method of claim 17, wherein the catalyst is fixed on a solid support.
26. The method of claim 17, wherein the catalyst is dissolved or dispersed in the ionic
15 liquid.
27. The method of claim 17, further comprising separating the disulfides from the ionic liquid.
28. The method of claim 27, wherein the disulfides are separated from the ionic liquid by distillation, decantation or gravity separation.
- 20 29. The method of claim 27, wherein the disulfides are separated from the ionic liquid by stripping with steam or air.
30. The method of claim 27, wherein the disulfides are separated from the ionic liquid by extraction with a suitable solvent.
31. The method of claim 1, further comprising oxidizing the mercaptides to disulfides,
25 separating the disulfides from the ionic liquid, and recycling the resulting de-sulfurized ionic liquid.
32. The method of claim 1, wherein the extent of reduction in mercaptan content is at least 10%, preferably 50% and most preferably 90%.
33. The method of claim 1, wherein the mercaptan reduction improves the copper strip
30 corrosion test value of the hydrocarbon feedstream by at least one value.

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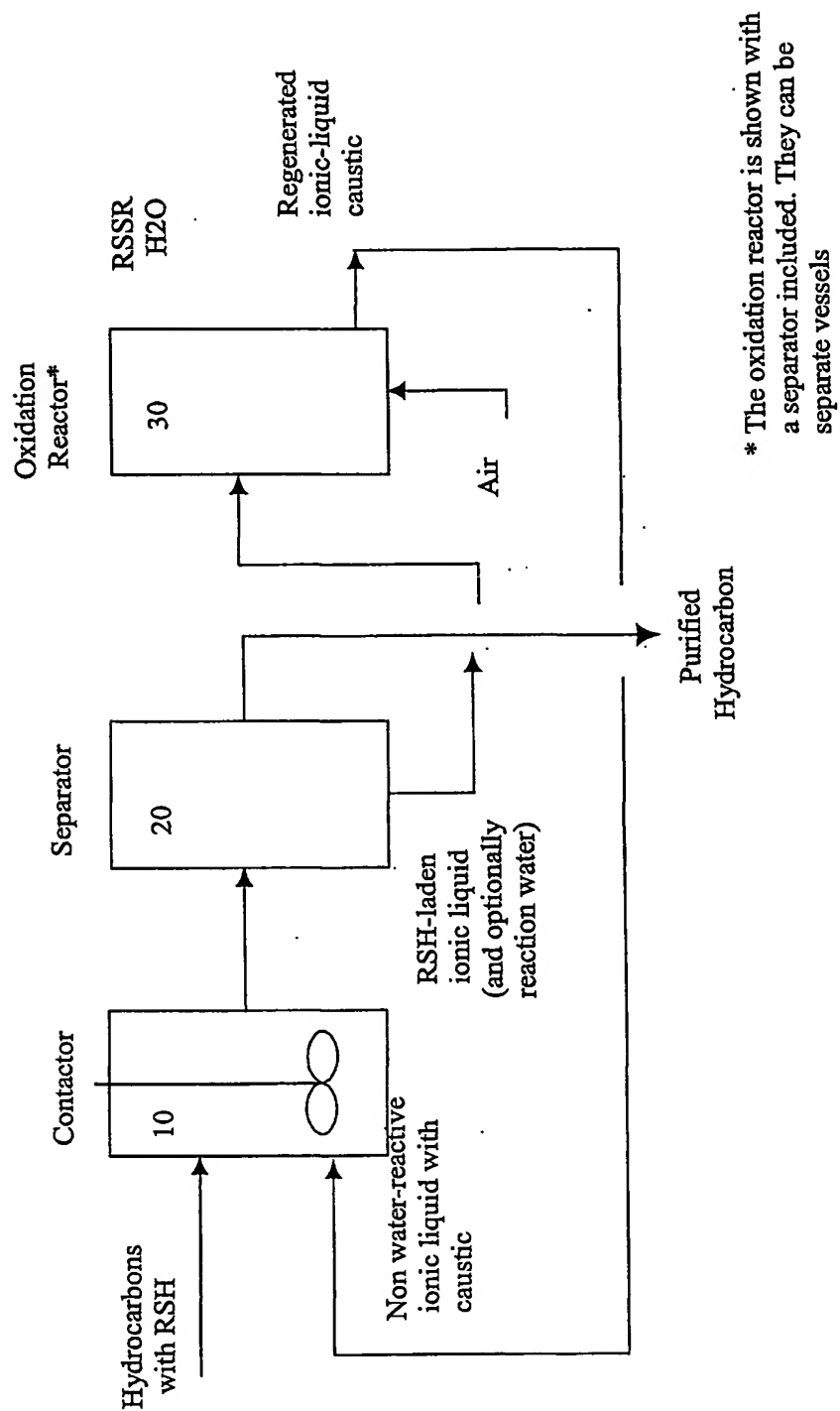


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/32211

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 19/00, 29/20, 27/00

US CL : 208/226, 227, 230, 235, 203, 189

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : C10G 19/00, 29/20, 27/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,997,731 A (SUAREZ) 07 December 1999 (07/12/99), See col 1, lines 14-32 and 55-60 and col 5, lines 37-44.	1-5, 8-13, 15-19, 26-33 ----- 20-22 and 25
Y	US 2,853,432 A (GLEIM ET AL) 23 September 1958 (23/09/58), See col 2, lines 7-9 and 68-69.	20-22 and 25
X	US 5,354,453 A (BHATIA) 11 October 1994 (11/10/94), See col 1, lines 1-10, col 3, lines 12-17, and col 4, line 9.	1, 5, 8, 13-15, 32, 33
X	US 5,683,574 A (MAZGAROV ET AL) 04 November 1997 (04/11/97), See abstract, col 3, lines 7-12 and 45-47, col 4, lines 1-5 and 25-37.	1-5, 8, 13-24, 26-29 and 31-33

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 JANUARY 2002

Date of mailing of the international search report

12 FEB 2002

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/52211

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 6,274,026 A (SCHUCKER ET AL) 14 August 2001 (14/08/01), See entire document.	1-33